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(54) **Conductive paste and glass circuit substrate**

(57) There is provided a conductive paste comprising a conductive component, a glass frit, and a vehicle, wherein: the glass frit comprises a main glass component and at least one selected from the group consisting of alumina (Al<sub>2</sub>O<sub>3</sub>), silica (SiO<sub>2</sub>), titania (TiO<sub>2</sub>), and zirconia (ZrO<sub>2</sub>).

The above conductive paste is capable of being baked at a low temperature with sufficient coloring, and suitable for forming a circuit on a glass substrate, and a glass circuit substrate suitable for the application in a defogging glass for an automobile window formed therewith.

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## Description

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

[0001] The present invention relates to a conductive paste, capable of being baked at a low temperature, suitable, for example, for the application of forming a circuit on a glass substrate, and a glass circuit substrate suitable for the application in a defogging glass for an automobile window formed therewith.

#### 2. Description of the Related Art

[0002] These days, a defogging glass for an automobile window for preventing fogging caused by dew condensation by forming a circuit (thick film electrode) on the surface of a glass by applying a conductive paste and generating heat by energizing the circuit (thick film electrode) has been used.

[0003] Recently, one having the rear surface of the circuit (thick film electrode) colored thickly has been preferred as the defogging glass for an automobile window.

[0004] Therefore, conventionally, thick coloring has been obtained in the rear surface of the circuit (thick film electrode) by forming the circuit (thick film electrode) with a conductive paste containing a pigment such as a chromium (Cr) oxide.

[0005] However, even in the case of using the above-mentioned conventional conductive paste containing a pigment such as a chromium (Cr) oxide, sufficient coloring cannot always be obtained, and thus a conductive paste having a better coloring property has increasingly been called for.

[0006] Moreover, a conductive paste having a pigment such as a chromium (Cr) oxide added gives rise to problems in difficulty in proceeding sintering, and a low bonding strength of the circuit (thick film electrode) on the glass surface.

[0007] As to the bonding strength, a method for promoting sintering by changing the sintering condition is conceivable, such as heightening the temperature at the time of sintering. However, since the glass itself comprising the circuit cannot endure a high temperature, there is a limit in heightening the sintering temperature.

### SUMMARY OF THE PRESENT INVENTION

[0008] To overcome the above described problems, preferred embodiments of the present invention provide a conductive paste, capable of being baked at a low temperature with sufficient coloring, and suitable for forming a circuit on a glass substrate, and a glass circuit substrate suitable for the application in a defogging glass for an automobile window formed therewith.

[0009] One preferred embodiment of the present invention provides a conductive paste comprising a con-

ductive component, a glass frit, and a vehicle, wherein: the glass frit comprises a main glass component and at least one selected from the group consisting of alumina ( $\text{Al}_2\text{O}_3$ ), silica ( $\text{SiO}_2$ ), titania ( $\text{TiO}_2$ ), and zirconia ( $\text{ZrO}_2$ ).

[0010] Since the above described conductive paste uses a glass frit prepared by adding at least one selected from the group consisting of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$  to a main glass component is used as the glass frit, color dimness can be prevented by restraining dispersion of Ag into a glass substrate, and thus sufficient coloring can be obtained without adding a pigment. Moreover, since a pigment needs not be added, a baking operation can be conducted at a low temperature efficiently.

[0011] As the conductive component, a part of a metal component can be contained in a resin state.

[0012] In the above described conductive paste, the conductive component may comprise

(a) Ag, or (b) that containing Ag and at least one selected from the group consisting of Cu, Pd and Pt, as the main substance.

[0013] Since (a) Ag, or (b) that containing Ag and at least one selected from the group consisting of Cu, Pd and Pt is used as the main substance comprising the conductive component, a conductive paste capable of forming an electrode having a sufficient conductivity for certain can be obtained, and thus it is advantageous.

[0014] In the above described conductive paste, nickel (Ni) or copper oxide ( $\text{CuO}$ ) may be added for adjusting the resistance.

[0015] Since nickel (Ni) or copper oxide ( $\text{CuO}$ ) is added for adjusting the resistance, a conductive paste having a desired characteristic can be obtained by adjusting the resistance, and thus the present invention can further be effective.

[0016] In the above described conductive paste, the glass frit may be prepared by adding at least one selected from the group consisting of alumina ( $\text{Al}_2\text{O}_3$ ) powders, silica ( $\text{SiO}_2$ ) powders, titania ( $\text{TiO}_2$ ) powders, and zirconia ( $\text{ZrO}_2$ ) powders to at least one selected from the group consisting of a Pb-containing glass, a Bi-containing glass, a Zn-containing glass, and Ba-containing glass, and adjusting the average particle size D50 in the range from 0.5 to 2.5  $\mu\text{m}$ .

[0017] Since a glass frit prepared by adding at least one selected from the group consisting of  $\text{Al}_2\text{O}_3$  powders,  $\text{SiO}_2$  powders,  $\text{TiO}_2$  powders, and  $\text{ZrO}_2$  powders to at least one selected from the group consisting of a Pb-containing glass, a Bi-containing glass, a Zn-containing glass, and Ba-containing glass, and adjusting the average particle size D50 in the range from 0.5 to 2.5  $\mu\text{m}$  is used, sufficient coloring can be obtained without adding a pigment further certainly as well as a baking operation can be conducted efficiently at a low temperature.

[0018] In the above described conductive paste, pow-

ders with a 40 to 90 mm<sup>2</sup>/g specific surface area may be used for the alumina (Al<sub>2</sub>O<sub>3</sub>) powders, the titania (TiO<sub>2</sub>) powders, and the zirconia (ZrO<sub>2</sub>) powders, powders with a 150 to 300 mm<sup>2</sup>/g specific surface area may be used for the silica (SiO<sub>2</sub>) powders, and at least one selected from the group consisting of the alumina (Al<sub>2</sub>O<sub>3</sub>) powders, the silica (SiO<sub>2</sub>) powders, the titania (TiO<sub>2</sub>) powders, and the zirconia (ZrO<sub>2</sub>) powders may be added so as to have a 5 to 60% by weight content ratio in the glass frit.

[0019] Since powders with a 40 to 90 mm<sup>2</sup>/g specific surface area are used for the Al<sub>2</sub>O<sub>3</sub> powders, the TiO<sub>2</sub> powders, and the ZrO<sub>2</sub> powders, powders with a 150 to 300 mm<sup>2</sup>/g specific surface area are used for the SiO<sub>2</sub> powders, and at least one selected from the group consisting of the Al<sub>2</sub>O<sub>3</sub> powders, the SiO<sub>2</sub> powders, the TiO<sub>2</sub> powders, and the ZrO<sub>2</sub> powders is added so as to have a 5 to 60% by weight content ratio in the glass frit, sufficient coloring can be obtained without adding a pigment as well as a baking operation can be conducted efficiently at a low temperature, and thus the present invention can further be effective.

[0020] In the above described conductive past, the glass frit may be contained in 2.0 to 8.0% by weight ratio.

[0021] In the case the glass frit is contained in 2.0 to 8.0% by weight ratio, a conductive paste having stable characteristics concerning the sintering property, the bonding property, and the coloring property can be obtained.

[0022] Another preferred embodiment of the present invention provides a glass circuit substrate, comprising a circuit on a glass substrate provided with the above described conductive paste.

[0023] The above described glass circuit substrate obtained by forming a circuit on a glass substrate with the conductive paste has a good coloring property and the excellent bonding strength of an electrode (circuit), and thus a high reliability can be obtained.

[0024] The above described glass circuit substrate may be served as a defogging glass for an automobile window.

[0025] Since the glass circuit substrate obtained by forming a circuit on a glass substrate with the conductive paste is used as a defogging glass for an automobile window, a defogging glass for an automobile with a high quality and a high reliability can be provided with sufficient coloring and the excellent bonding property with a glass of a circuit.

[0026] Other features and advantages of the present invention will become apparent from the following description of the invention which refers to the accompanying drawings.

## BRIEF DESCRIPTION OF DRAWINGS

[0027]

FIG. 1A is a graph showing the relationship between the glass frit addition amount and the bonding strength, and FIG. 1B is a chart showing the relationship between the glass frit addition amount and the coloring evaluation.

FIG. 2A is a graph showing the relationship between the SiO<sub>2</sub> addition amount to the glass frit and the bonding strength, and FIG. 2B is a chart showing the relationship between the SiO<sub>2</sub> addition amount and the coloring evaluation.

FIG. 3A is a graph showing the relationship between the glass frit particle size and the bonding strength, and FIG. 3B is a chart showing the relationship between the glass frit particle size and the coloring evaluation.

FIG. 4A is a graph showing the relationship between the specific surface area of SiO<sub>2</sub> added to the glass frit and the bonding strength, and FIG. 4B is a chart showing the relationship between the SiO<sub>2</sub> specific surface area and the coloring evaluation.

FIG. 5A is a graph showing the relationship between the addition amount of the oxide (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub>) added to the glass frit and the bonding strength, and FIG. 5B is a chart showing the relationship between the oxide (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub>) addition amount and the coloring evaluation.

FIG. 6A is a graph showing the relationship between the specific surface area of the oxide (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub>) added to the glass frit and the bonding strength, and FIG. 6B is a chart showing the relationship between the oxide (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub>) specific surface area and the coloring evaluation.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0028] Glass frits were produced by the following procedure.

[0029] Glass cullets were obtained by melting glass materials each containing Pb, Bi, Zn and Ba at high temperature, followed by quenching for vitrification.

[0030] Then, the glass cullets were coarsely pulverized until having a 5 to 10 μm average particle size with a roll crusher, a stone crusher, or the like.

[0031] Glass frits were obtained by adding fine powders of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub> to the coarsely pulverized glass cullets, and finely pulverizing and mixing with a pot mill, a planetary ball mill, or the like.

[0032] Conductive pastes were produced by mixing 1 to 10% by weight of the glass frits, 69 to 78% by weight of silver (Ag) powders, 1% by weight of nickel powders,

1% by weight of copper oxide powders, and 19% by weight of an organic vehicle, and kneading and dispersing with a triple roll.

[0033] As the organic vehicle, one prepared by dissolving 8% by weight of a cellulose resin in terpineol was used.

[0034] The nickel powders and the copper oxide powders were added for adjusting the resistance value.

[Production of samples for measuring the bonding strength]

[0035] By printing the conductive pastes produced as mentioned above onto the surface of slide glass substrates (soda-lime glass, 260 mm × 760 mm × 1.4 mm) in a 2 mm square shape, drying at 150°C for 10 minutes, and baking at a 600°C for one minute (in-out: 5 minutes) condition so as to form electrodes.

[0036] Then, the slide glass substrates with the electrodes formed were placed on plates heated to 150°C, and lead terminals were soldered on the electrodes.

[0037] As the lead terminals, an L-shaped solder copper line having a 0.6 mm diameter was used. A solder containing Sn-Pb-Ag was used as the solder, and a flux prepared by dissolving rosin in isopropyl alcohol was used as the flux.

[Production of samples for measuring the coloring thickness]

[0038] Similar to the case of the samples for measuring the bonding strength, samples for measuring the coloring thickness were produced by printing the conductive pastes onto the surface of slide glass substrates in a 10 mm diameter circle pattern, drying at 150°C for 10 minutes, and baking at a 600°C for one minute (in-out: 5 minutes) condition.

[Measurement of the bonding strength]

[0039] With the samples for measuring the bonding strength produced as mentioned above, the bonding strength of the electrodes with the slide glass substrates was measured. In measuring the bonding strength, a lead line was pulled with a 20 mm/min rate in the perpendicular direction with respect to the surface of the slide glass having the above-mentioned electrode formed. The strength at which the electrode was peeled off is defined to be the bonding strength.

[0040] The results are shown in FIG. 1A to FIG. 6A. Measurement of the bonding strength was conducted for each 20 samples (n=20). The average value of the measured values is shown in FIGS. 1A, 2A, 3A, 4A, 5A and 6A.

[0041] The indication of Pb-containing, Bi-containing, Zn-containing and Ba-containing in each line drawing shows the kind of the glass component comprising each glass frit.

[Ranking of the coloring thickness]

[0042] The coloring thickness of each sample was ranked by the visual observation of the samples prepared by printing the conductive pastes in a 10 mm diameter circle pattern and baking for forming the electrodes, and the comparison with standard samples.

[0043] Concretely, standard samples (JIS Z 8729) in 3 grades were produced, and numbered as No. 1, No. 2, and No. 3 from the thicker one as shown in Table 1. By visually observing each sample, the coloring thickness was evaluated by putting ⊙ for one obtained a coloring thickness of No. 1 or more, ○ for one obtained a coloring thickness of No. 2 or more, △ for one obtained a coloring thickness of No. 3 or more, and ? for one obtained a coloring thickness thinner than No. 3.

[Table 1]

	No.	*L	*U	*V
Thicker ↑ Thinner	1	21.84	32.70	24.50
	2	28.67	43.67	33.48
	3	38.50	50.22	45.67

\*L: psychometric lightness

\*U: psychometric chroma coordinate

\*V: psychometric chroma coordinate

[0044] The results thereof (coloring evaluation) are also shown in FIGS. 1B, 2B, 3B, 4B, 5B and 6B. In the column (table) of these drawings, the position of each frame corresponds with the horizontal axis (showing the component addition amount, the specific surface area, or the like) of each line drawing of FIG. 1A to FIG. 6A showing the bonding strength for facilitating the understanding. For example, the second column from the left in FIG. 1B corresponds with the 2% by weight glass frit addition amount in FIG. 1A, and the right end column in FIG. 1B corresponds with the 10% by weight glass frit addition amount in FIG. 1A.

[0045] The indication of Pb-containing, Bi-containing, Zn-containing, and Ba-containing in the column of the coloring evaluation shows the kind of the glass component comprising each glass frit.

[Evaluation of the bonding strength and the coloring thickness]

[0046] Evaluation of the bonding strength and the coloring thickness will be explained with reference to FIG. 1 to FIG. 6.

[0047] FIG. 1 shows the relationship between the glass frit addition amount, and the bonding strength and coloring in the case the addition amount of the glass

frits is changed, using glass frits not containing  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ .

[0048] As shown in FIG. 1, with a less than 2.0% by weight glass frit addition amount, the bonding strength of the electrode is insufficient in each glass.

[0049] Moreover, with a more than 8.0% by weight glass frit addition amount, it was difficult to solder a lead line for measuring the bonding strength.

[0050] Therefore, the glass frit addition amount is preferably in the range from 2.0 to 8.0% by weight. Since the most stable characteristic can be obtained by having the glass frit addition amount in the range from 4.0 to 6.0% by weight, and thus it is preferable.

[0051] Further, concerning coloring, tendency of difficulty in obtaining sufficient coloring with a small glass frit addition amount and availability of good coloring with a large glass frit addition amount was found, but the results show that it is difficult to obtain good evaluation in both bonding strength and coloring because  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$  are not added.

[0052] FIG. 2 shows the relationship between the  $\text{SiO}_2$  addition amount, and the bonding strength and coloring in the case of further adding  $\text{SiO}_2$  to the glass components comprising the glass frits.

[0053] The addition amount of the glass frits with respect to the conductive pastes was fixed to be 4.0% by weight.

[0054] As shown in FIG. 2, it is observed that in the case  $\text{SiO}_2$  is added in the range up to 60% by weight content ratio in the glass frit, a necessary bonding strength can be obtained, but the bonding strength is drastically declined if it exceeds 60% by weight. This is because the electrodes can hardly be baked with a too much  $\text{SiO}_2$  addition amount.

[0055] Moreover, concerning the coloring evaluation, it is observed that the effect is achieved from more than 5% by weight  $\text{SiO}_2$  addition amount, and thicker coloring can be obtained with a larger  $\text{SiO}_2$  addition amount.

[0056] The bonding strength and the coloring can be obtained most stably in the 15 to 45% by weight  $\text{SiO}_2$  addition amount range.

[0057] FIG. 3 shows the relationship between the glass frit particle size, and the bonding strength and coloring in the case the particle size of the glass frits is changed, using glass frits not containing  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ .

[0058] The addition amount of the glass frits with respect to the conductive pastes was fixed to be 4.0% by weight.

[0059] As shown in FIG. 3, it is observed that the bonding strength tends to decline with a larger glass frit particle size, and with a more than 2.5  $\mu\text{m}$  particle size, the strength is declined to 15N or less.

[0060] Concerning coloring, influence of the glass frit particle size was not found.

[0061] FIG. 4 shows the relationship between the specific surface area of  $\text{SiO}_2$  added to the glass components comprising the glass frits, and the bonding

strength and coloring.

[0062] The addition amount of  $\text{SiO}_2$  with respect to the glass frits was fixed to be 45% by weight, and the addition amount of the glass frits with respect to the conductive pastes was fixed to be 4.0% by weight.

[0063] As shown in FIG. 4, with a larger specific surface area of the added  $\text{SiO}_2$ , the bonding strength is increased and the coloring property is improved.

[0064] Moreover, it was observed that the bonding strength is drastically declined with a less than 150  $\text{mm}^2/\text{g}$  specific surface area.

[0065] Although the  $\text{SiO}_2$  specific surface area was evaluated only to 300  $\text{mm}^2/\text{g}$ , it is considered that a good result can be obtained with a larger specific surface area.

[0066] FIG. 5 shows the relationship between the oxide addition amount, and the bonding strength and coloring in the case oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ ) are further added to the glass components comprising the glass frits.

[0067] The addition amount of the glass frits with respect to the conductive pastes was fixed to be 4.0% by weight.

[0068] As shown in FIG. 5, in the case  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$  are added in the range up to 60% by weight content ratio in the glass frit, a necessary bonding strength can be obtained, but the bonding strength is drastically declined if it exceeds 60% by weight. This is because the electrodes can hardly be baked with a too much oxide ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ ) addition amount.

[0069] Moreover, concerning the coloring evaluation, it is observed that the effect is achieved from more than 5% by weight oxide ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ ) addition amount, and thicker coloring can be obtained with a larger oxide addition amount.

[0070] The bonding strength and the coloring can be obtained most stably in the 15 to 45% by weight oxide ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ ) addition amount range.

[0071] FIG. 6 shows the relationship between the specific surface area of the oxide ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ ) added to the glass components comprising the glass frits, and the bonding strength and coloring.

[0072] The addition amount of the oxide ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ ) with respect to the glass frits was fixed to be 45% by weight, and the addition amount of the glass frits with respect to the conductive pastes was fixed to be 4.0% by weight.

[0073] As shown in FIG. 6, with a larger specific surface area of the added oxide ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ ), the bonding strength is increased and the coloring property is improved.

[0074] Moreover, the bonding strength is declined as well as coloring tends to be thinner with a less than 40  $\text{mm}^2/\text{g}$  specific surface area.

[0075] Although the case of using silver powders as the conductive component has been explained in the above-mentioned embodiments, metal powders comprising Ag and at least one selected from the group con-

sisting of Cu, Pd, and Pt can also be used as the conductive component. Further, other substances can be contained as the conductive component.

[0076] Moreover, although the case including nickel powders and copper oxide powders for adjusting the resistance value has been explained in the above-mentioned embodiments, in some cases, the nickel powders and the copper oxide powders need not be added.

[0077] Furthermore, by forming a circuit on a glass substrate, using the conductive paste according to the present invention, a defogging glass for an automobile having a large electrode bonding strength and a sufficient coloring thickness can be obtained. Since the production method and the concrete configuration of a defogging glass for an automobile are not different from conventional ones, explanation thereof is omitted.

[0078] While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that the forgoing and other changes in form and details may be made therein without departing from the spirit of the invention.

#### Claims

1. A conductive paste comprising a conductive component, a glass frit, and a vehicle, wherein:

the glass frit comprises a main glass component and at least one selected from the group consisting of alumina ( $\text{Al}_2\text{O}_3$ ), silica ( $\text{SiO}_2$ ), titania ( $\text{TiO}_2$ ), and zirconia ( $\text{ZrO}_2$ ).

2. The conductive paste according to claim 1, wherein the conductive component comprises

(a) Ag, or  
(b) that containing Ag and at least one selected from the group consisting of Cu, Pd and Pt

as the main substance.

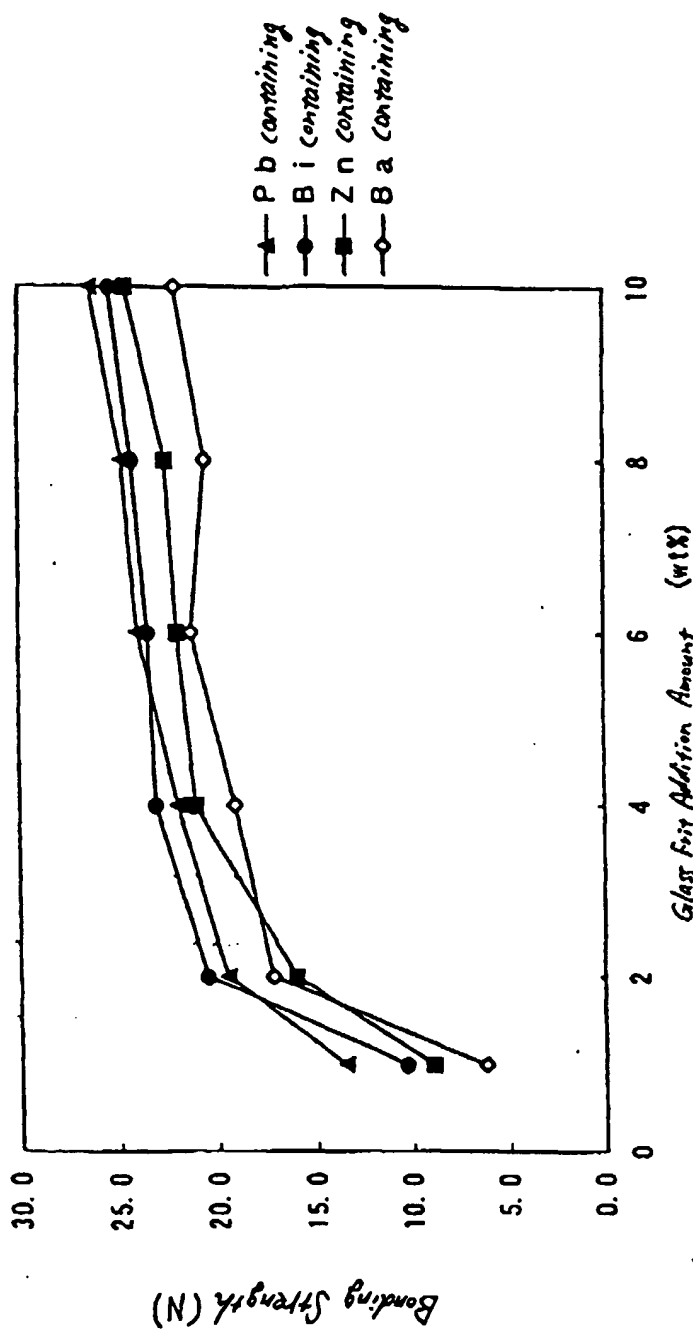
3. The conductive paste according to claim 1 or 2, wherein nickel (Ni) or copper oxide ( $\text{CuO}$ ) is added for adjusting the resistance.

4. The conductive paste according to one of claims 1 to 3, wherein the glass frit is prepared by adding at least one selected from the group consisting of alumina ( $\text{Al}_2\text{O}_3$ ) powders, silica ( $\text{SiO}_2$ ) powders, titania ( $\text{TiO}_2$ ) powders, and zirconia ( $\text{ZrO}_2$ ) powders to at least one selected from the group consisting of a Pb-containing glass, a Bi-containing glass, a Zn-containing glass, and Ba-containing glass, and adjusting the average particle size D50 in the range from 0.5 to 2.5  $\mu\text{m}$ .

5. The conductive paste according to one of claims 1

to 4, wherein powders with a 40 to 90  $\text{mm}^2/\text{g}$  specific surface area are used for the alumina ( $\text{Al}_2\text{O}_3$ ) powders, the titania ( $\text{TiO}_2$ ) powders, and the zirconia ( $\text{ZrO}_2$ ) powders, powders with a 150 to 300  $\text{mm}^2/\text{g}$  specific surface area are used for the silica ( $\text{SiO}_2$ ) powders, and at least one selected from the group consisting of the alumina ( $\text{Al}_2\text{O}_3$ ) powders, the silica ( $\text{SiO}_2$ ) powders, the titania ( $\text{TiO}_2$ ) powders, and the zirconia ( $\text{ZrO}_2$ ) powders is added so as to have a 5 to 60% by weight content ratio in the glass frit.

6. The conductive paste according to one of claims 1 to 5, wherein the glass frit is contained in 2.0 to 8.0% by weight ratio.
7. A glass circuit substrate, comprising a circuit on a glass substrate provided with the conductive paste according to one of claims 1 to 6.
8. The glass circuit substrate according to claim 7, wherein the glass circuit substrate is a defogging glass for an automobile window.



**Fig. 1B**

Coloring Evaluation

P b containing	○	○	○	○	○	○	○	○
B i containing	△	○	○	○	○	○	○	○
Z n containing	x	△	○	○	○	○	○	○
B a containing	x	△	△	○	○	○	○	○

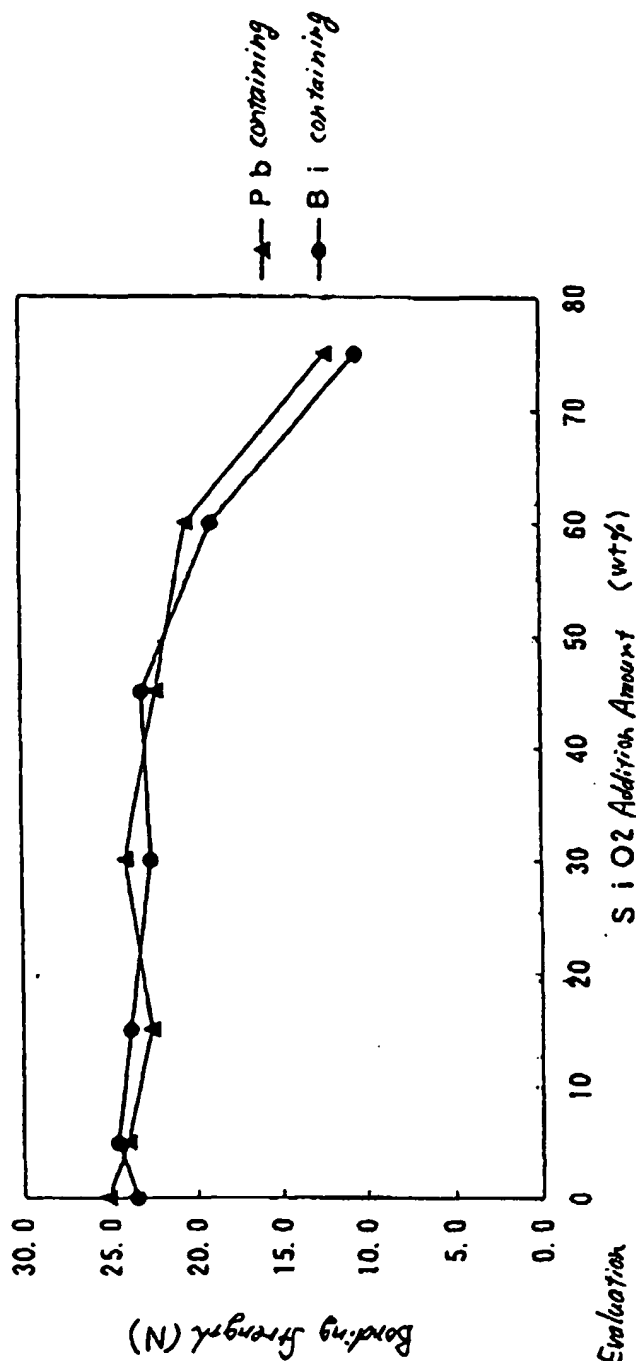


Fig. 2A

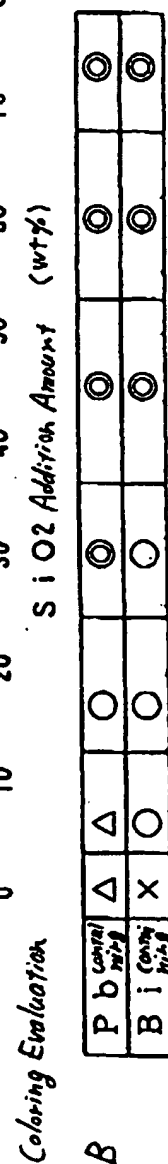


Fig. 2B



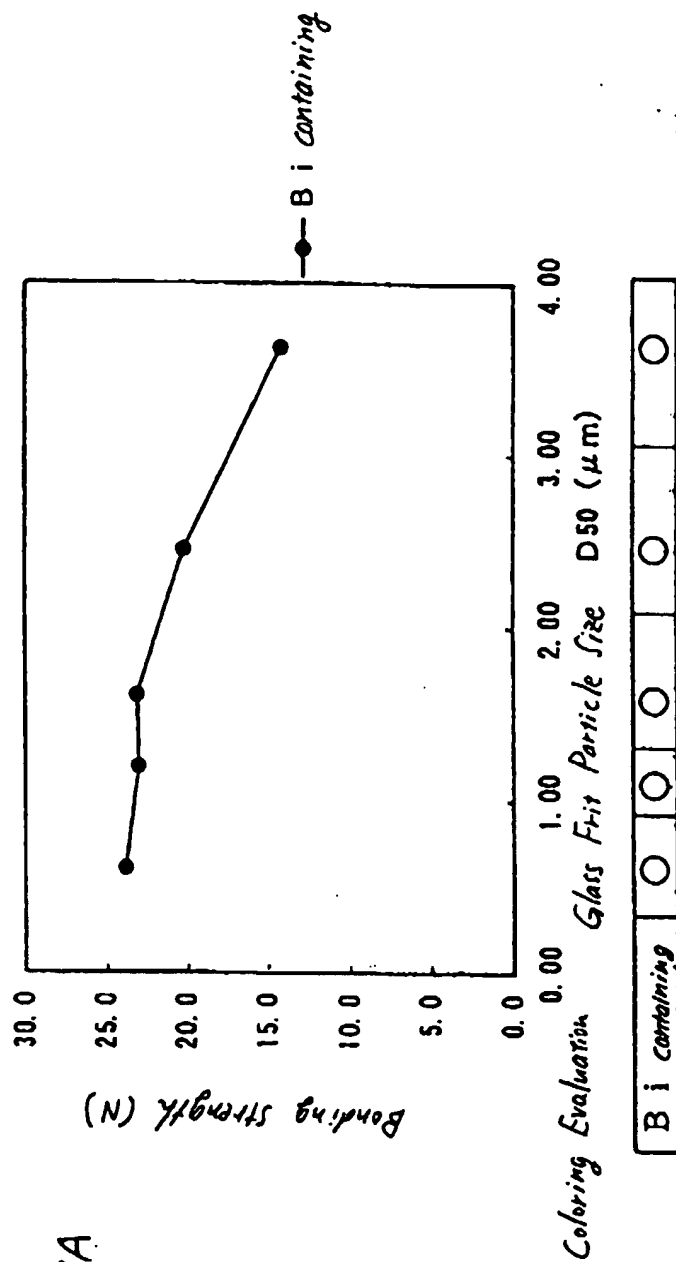


Fig. 3A

Fig. 38

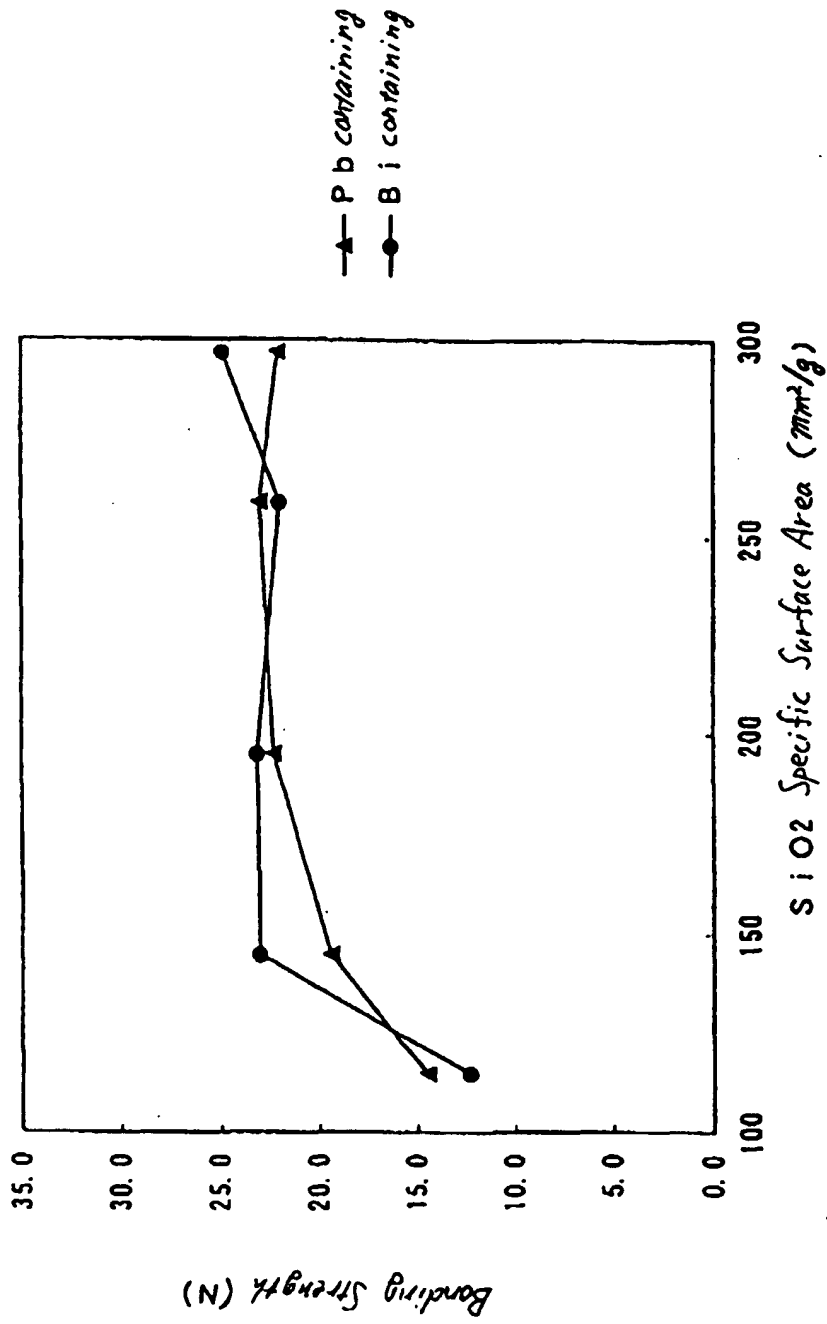


Fig. 4A

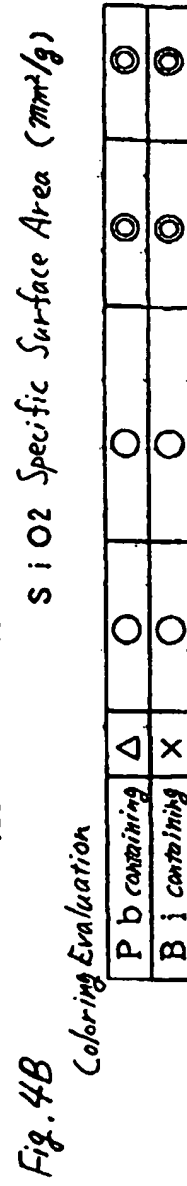


Fig. 4B

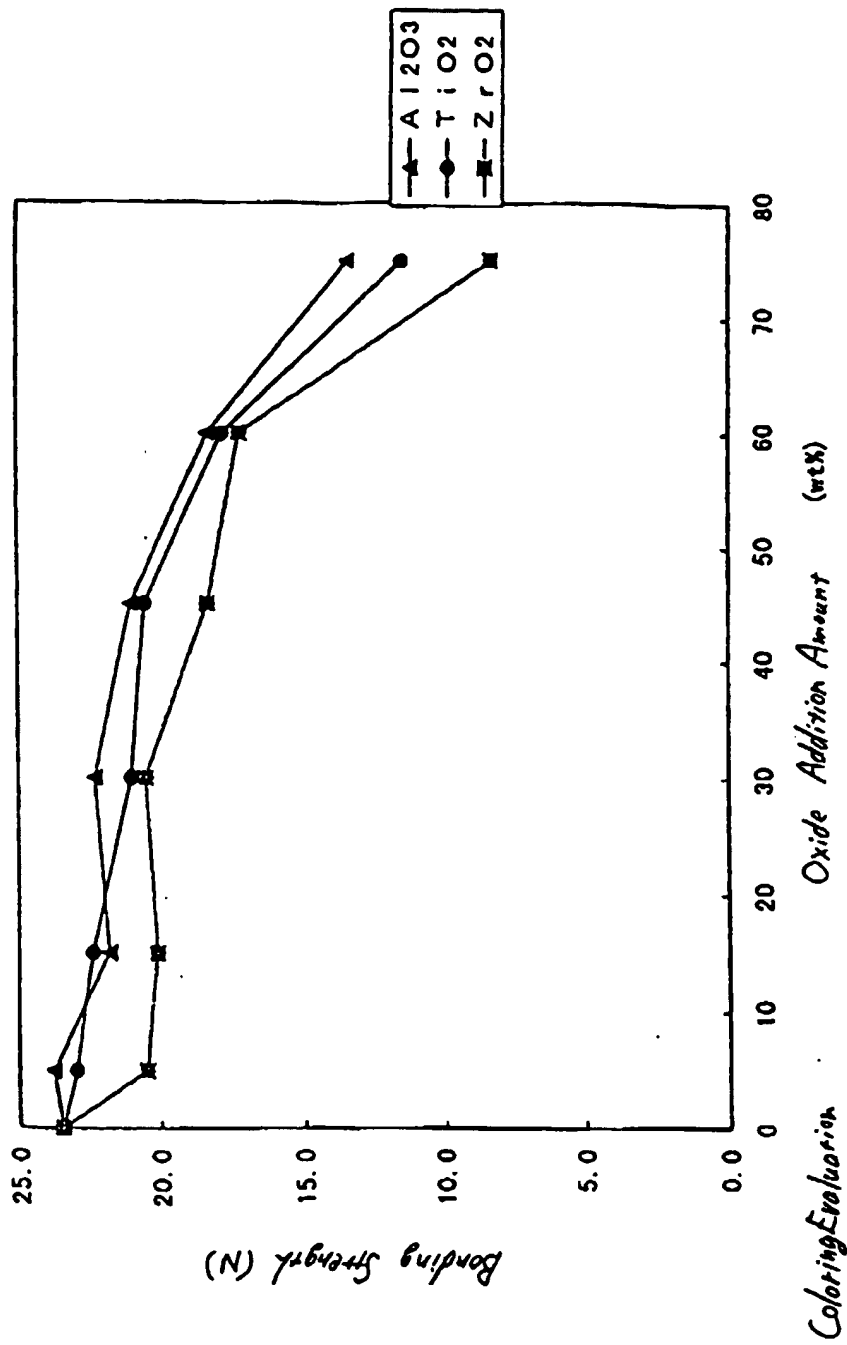


Fig. 5A

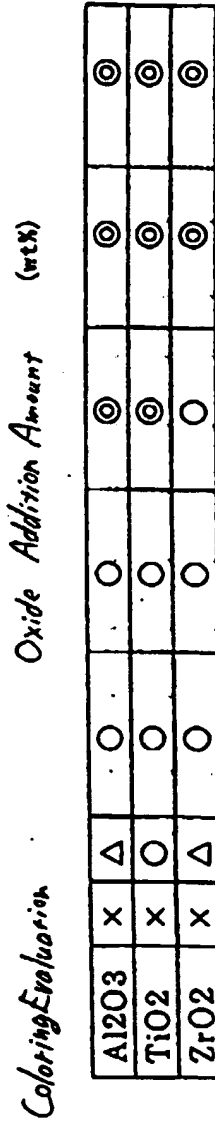


Fig. 5B

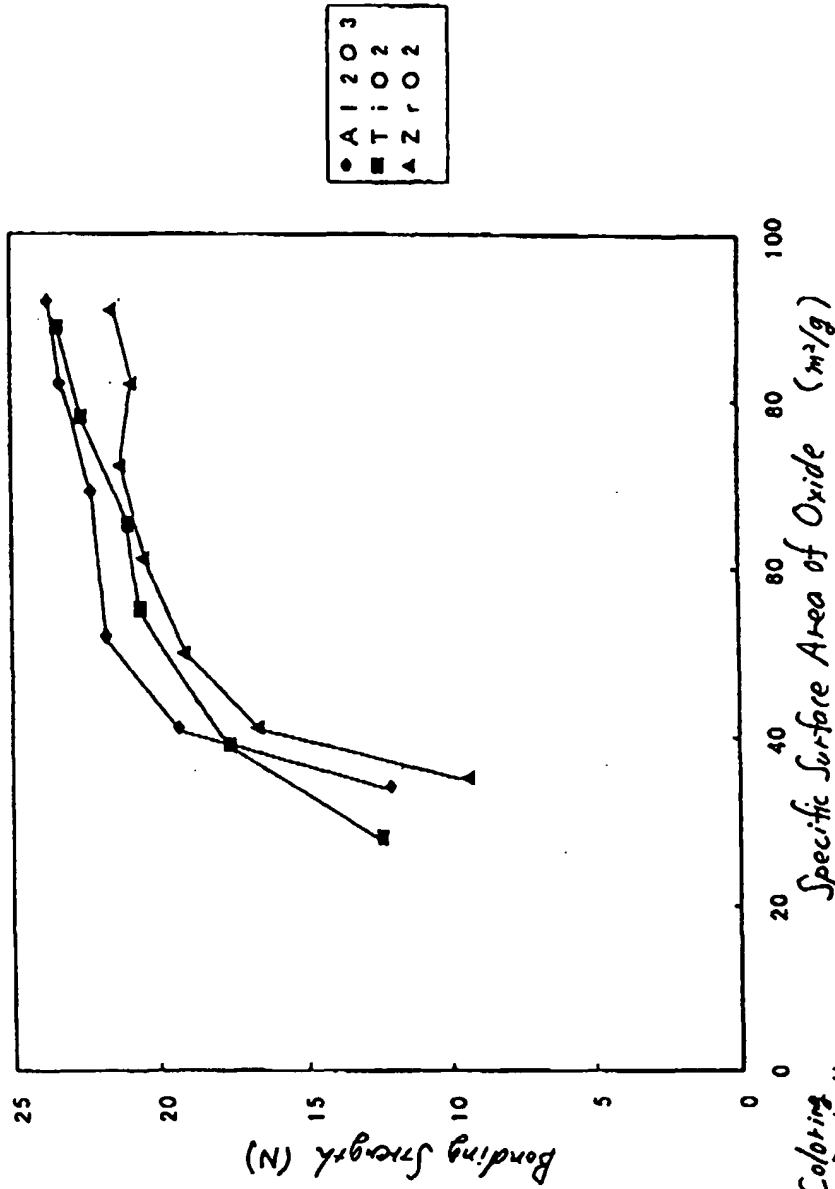


Fig. 6B

	Coloring Evaluation									
	0	20	40	60	80	100	120	140	160	180
Al <sub>2</sub> O <sub>3</sub>										
TiO <sub>2</sub>										
ZrO <sub>2</sub>										



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(54) **Conductive paste and glass circuit substrate**

(57) There is provided a conductive paste comprising a conductive component, a glass frit, and a vehicle, wherein: the glass frit comprises a main glass component and at least one selected from the group consisting of alumina (Al<sub>2</sub>O<sub>3</sub>), silica (SiO<sub>2</sub>), titania (TiO<sub>2</sub>), and zirconia (ZrO<sub>2</sub>).

The above conductive paste is capable of being baked at a low temperature with sufficient coloring, and suitable for forming a circuit on a glass substrate, and a glass circuit substrate suitable for the application in a defogging glass for an automobile window formed therewith.



European Patent  
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# EUROPEAN SEARCH REPORT

Application Number  
EP 99 11 4680

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 5 378 408 A (CARROLL ALAN F ET AL) 3 January 1995 (1995-01-03) * the whole document *	1,2,4-8	H01B1/16
X	US 5 346 651 A (OPROSKY JOANNA ET AL) 13 September 1994 (1994-09-13) * the whole document *	1,2,4-8	
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 09, 31 July 1998 (1998-07-31) & JP 10 106346 A (TANAKA KIKINZOKU KOGYO KK), 24 April 1998 (1998-04-24) * abstract *	1,2,4-8	
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 05, 30 May 1997 (1997-05-30) & JP 09 017232 A (TANAKA KIKINZOKU INTERNATL KK), 17 January 1997 (1997-01-17) * abstract *	1-4	
X	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 05, 30 June 1995 (1995-06-30) & JP 07 037420 A (TDK CORP), 7 February 1995 (1995-02-07) * abstract *	1-4	TECHNICAL FIELDS SEARCHED (Int.Cl.7)  H01B
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>25 August 2000</b>	Examiner <b>Drouot-Onillon, M-C</b>
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 (3.82) (PulC01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 11 4680

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
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25-08-2000

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5378408	A	03-01-1995	CN 1103057 A,B	31-05-1995
			DE 69406455 D	27-11-1997
			DE 69406455 T	26-03-1998
			EP 0711255 A	15-05-1996
			JP 9501136 T	04-02-1997
			KR 173418 B	18-02-1999
			WO 9504005 A	09-02-1995
			US 5468695 A	21-11-1995
US 5346651	A	13-09-1994	AT 163488 T	15-03-1998
			BR 9403375 A	09-05-1995
			CA 2131138 A	01-03-1995
			DE 69408609 D	02-04-1998
			DE 69408609 T	18-06-1998
			EP 0640993 A	01-03-1995
			ES 2115825 T	01-07-1998
			GR 3026652 T	31-07-1998
			JP 7105723 A	21-04-1995
			US 5417745 A	23-05-1995
JP 10106346	A	24-04-1998	NONE	
JP 09017232	A	17-01-1997	NONE	
JP 07037420	A	07-02-1995	NONE	

EPO FORM P4429

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82